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DYSPROSIUM

[7429-91-6]

Symbol Dy; atomic number 66; atomic weight 162.50; a lanthanide series, inner transition, rare earth metal; electron configuration $[\text{Xe}]4f^95d^16s^2$; atomic volume $19.032 \text{ cm}^3/\text{g}$. atom; atomic radius $1.773\text{\AA}$; ionic radius $0.908\text{\AA}$; most common valence state +3.

History, Occurrence, and Uses

Dysprosium was discovered in 1866 by Boisbaudran. It occurs in the earth's crust associated with other rare earth metals. It is found in the minerals, xenotime YPO_4 , gadolinite, euxemite and monazite $(\text{Ce}, \text{La}, \text{Th})\text{PO}_4$. The concentration of dysprosium in seawater is 0.9 ng/L and in the earth's crust 5.2 mg/kg .

Dysprosium is used in nuclear reactor fuels to measure neutron flux. It also is used as a fluorescence activator in phosphors.

Physical Properties

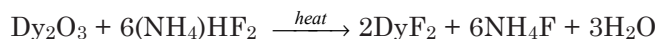
Silvery metal; hexagonal crystals; density 8.559 g/cm^3 ; melts at $1,411^\circ\text{C}$; vaporizes at $2,561^\circ\text{C}$; electrical resistivity 92.6 microhm-cm at 25°C ; Poisson's ratio 0.243; Young's modulus $0.644 \times 10^6 \text{ g/cm}^2$; soluble in dilute acids.

Thermochemical Properties

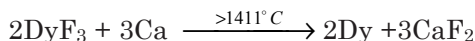
ΔH_f°	0.0
S°	$75.6 \text{ J/degree mol}$
C_p	$27.7 \text{ J/degree mol}$
ΔH_{fus}	2.58 kcal/mol

Production

Dysprosium is produced mostly from its minerals xenotime, gadolinite, euxenite, and monazite. The metal is obtained as a by-product in the commercial production of yttrium. Finely ground ore is heated with excess concentrated sulfuric acid which converts yttrium and the other rare-earth metals into their sulfates. The water-soluble sulfates are separated from silica and other unreacted minerals with cold water. The solution is then filtered. Yttrium and other rare-earth metals in the aqueous extract are separated by displacement ion exchange techniques. Copper sulfate or zinc sulfate pretreated with $1 \text{ M H}_2\text{SO}_4$ is used as cation exchange resin and ammonium EDTA solution as eluting agent in the process. The separated fractions are treated with oxalic acid. Insoluble oxalates are obtained. Dysprosium and yttrium oxalates obtained from the fraction containing these metals are decomposed to their oxides by roasting at $800\text{--}900^\circ\text{C}$. The dysprosium sesquioxide, Dy_2O_3 , is then converted to dysprosium fluoride, DyF_3 , by heating with ammonium hydrogen fluoride:



The fluoride salt is reduced to dysprosium by heating above the melting point of dysprosium with calcium in argon atmosphere in a tungsten or tantalum vessel:



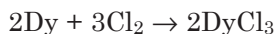
Dysprosium obtained this way may contain small quantities of tungsten or tantalum which may leach out of the reaction vessel, dissolving into molten dysprosium.

Minerals such as euxenite, fergusonite, samarskite, polycrase and loparite are highly refractory and complex in nature. These minerals may be opened up by treatment with hydrofluoric acid. While metals such as niobium, tantalum and titanium form soluble fluorides, rare earth elements form an insoluble residue of their fluorides. Such insoluble fluorides are filtered out of solution and digested with hot concentrated sulfuric acid. The rare earth sulfates formed are dissolved in cold water and thus separated from the insoluble mineral impurities. Rare earth elements in the aqueous solution are then separated by displacement ion exchange techniques outlined above.

Dysprosium is often produced from gadolinite, $\text{Be}_2\text{Fe}(\text{Y})_2\text{Si}_2\text{O}_{10}$, an important ore of the metal. The pulverized mineral is either digested with a mixture of hot nitric and hydrochloric acids or fused with caustic soda. When digested with acid, the lanthanide elements along with beryllium and iron are extracted into the acid solution leaving behind insoluble siliceous residue. The solution is diluted and filtered. It is then treated with oxalic acid to precipitate out rare earth oxalates, thus separating these elements from iron and beryllium in the solution. The oxalates are now roasted at 800–900°C to form corresponding oxides, which are then redissolved in hydrochloric acid to separate from any siliceous matter present. The filtered chloride solutions of dysprosium and other rare earth metals are subjected to ion exchange separation, as discussed above. If caustic fusion process is applied, gadolinite forms water-soluble sodium silicate and insoluble rare earth hydroxides. The fused melt is treated with water and filtered. The insoluble hydroxides are dissolved in dilute acids and subjected to the displacement ion exchange separation discussed above.

Reactions

At ordinary temperature, dysprosium is relatively stable in air. However, when heated with oxygen it forms dysprosium sesquioxide, Dy_2O_3 . With halogens, dysprosium reacts slowly at room temperature forming dysprosium trihalides:

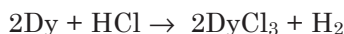


The reaction is vigorous above 200°C.

Dysprosium combines with several nonmetals at high temperatures forming binary compounds with varying compositions. Heating with hydrogen produces dysprosium dihydride, DyH_2 , and dysprosium trihydride, DyH_3 . With sulfur, several sulfides have been synthesized that have the compositions

DyS, DyS₂, Dy₂S₃, and Dy₅S₇. Heating with boron and carbon yields several borides and carbides, respectively, that have compositions DyB₂, DyB₄, DyB₆, DyB₁₂, Dy₃C, and Dy₂C₃. It forms dysprosium nitride, DyN, and dysprosium phosphide, DyP, when heated with nitrogen and phosphorus respectively. Dysprosium also combines with many metals such as gallium, zinc, manganese, indium, arsenic, antimony, selenium, silicon, germanium, platinum, and polonium. It also combines with many metals at elevated temperatures.

Dysprosium dissolves in most mineral acids with the evolution of hydrogen:



The action of 1:1 HNO₃ is relatively slow.

Analysis

Dysprosium may be analyzed by AA, ICP, ICP–MS and x-ray fluorescence and diffraction techniques.

Toxicity

Dysprosium has low acute toxicity. Its soluble salts exhibit low toxicity in experimental animals when administered by intravenous route. The effects were degeneration of the liver and spleen.

EINSTEINIUM

[7429-92-7]

Symbol Es; atomic number 99; atomic weight 252; a radioactive transuranium, actinide series, manmade element; electron configuration [Rn]5f¹¹7s²; the most stable isotope Es-254. Isotopes, their half-lives and the mode of decay are as follows:

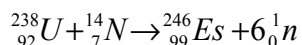
Isotopes	Half-life	Mode of Decay
Es-245	75 sec	Orbital electron capture, Alpha decay
Es-246	7.3 min	Orbital electron capture, Alpha decay
Es-248	25 min	Orbital electron capture, Alpha decay
Es-249	2 hr	Orbital electron capture, Alpha decay
Es-250	8 hr	Orbital electron capture
Es-251	1.5 days	Orbital electron capture, Alpha decay
Es-252	140 days	Alpha decay
Es-254	276 days	Alpha decay
Es-254m (Metastable isomer)	39.3 hr	Beta decay, Alpha decay
Es-255	39.8 days	Beta decay, Alpha decay

History, Occurrence, and Uses

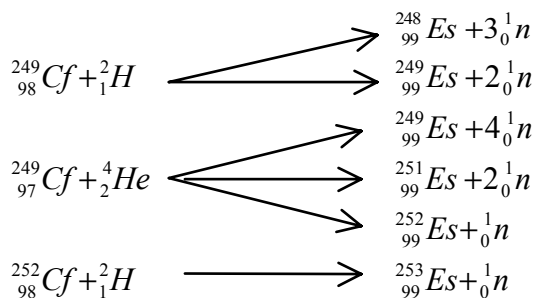
The first isotope of this element having mass number 253 and half-life 20 days was detected in 1952 in the Pacific in debris from the first thermonuclear explosion. The isotope was an alpha emitter of 6.6 MeV energy, chemically analogous to the rare earth element holmium. Isotope 246, having a half-life 7.3 minutes, was synthesized in the Lawrence Berkeley Laboratory cyclotron in 1954. The element was named Einsteinium in honor of Albert Einstein. Only microgram amounts have been synthesized. The element has high specific alpha activities. It may be used as a tracer in chemical studies. Commercial applications are few.

Production

The isotope Es-246 may be synthesized in a cyclotron by bombarding uranium-238 with nitrogen ions:



Isotopes of masses 248, 249, 250, 251 and 252 may be prepared from berkelium-249 or californium-249 by bombardment with alpha particles or deuterium ions:



Heavier isotopes Es-253, Es-254 and Es-255 can be produced in a nuclear reactor by multiple neutron capture reactions that may occur when uranium, neptunium and plutonium isotopes are irradiated under intense neutron flux. These and other isotopes also are produced during thermonuclear explosions.

Separation /Analysis

Einsteinium isotopes are separated on an ion exchange column and eluted with a solution of ammonium citrate. Radioactive isotopes are identified by an activity detector.

element; lanthanide series, inner-transition metal; electron configuration [Xe]4f¹¹5d¹6s²; metallic radius (CN 12) 1.758Å; atomic volume 18.49 cc/mol; naturally occurring stable isotopes and their percent abundances: Er-166 (33.41%), Er-168(27.07%), Er-167(22.94%), Er-170 (14.88%), Er-164(1.56%), Er-162 (0.136%); several radioisotopes have been prepared.

History, Occurrence and Uses

Erbium oxide was separated and obtained from the rare earth oxide, yttria in 1842 by Mosander. Urbain and James independently separated this oxide from other rare earth oxide mixtures in 1905. The pure metal was produced by Klemm and Bommer in 1934 in powdered form.

Erbium is distributed in nature, commonly occurring as mixtures with other lanthanide elements. A common mineral is gadolinite. Its concentration in the earth's crust is 2.8 mg/kg and in sea water is about 0.9 ng/L.

Physical Properties

Silvery metal; hexagonal, close-packed crystals; dark grey powder; rose colored solution; in lump form the metal is stable at ordinary temperatures; in the finely-divided state it ignites in air; density 9.066 g/cm³; melts at 1,529°C; vaporizes at 2,863°C; vapor pressure 0.4 torr at its melting point; electrical resistivity 87 microhm-cm at 25°C and 205 microhm-cm at 1,000°C; Poisson's ratio 0.238; Young's modulus 2.96x10¹¹ dynes/cm²; Effective magnetic moment 9.9 Bohr magnetons (at 25°C) (paramagnetic, changes to antiferromagnetic at -189°C and ferromagnetic at -253°C); insoluble in water; soluble in acid.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔG_f° (cry)	0.0
S° (cry)	17.49 cal/degree mol
C_p (cry)	6.72 cal/degree mol
ΔH_f° (g)	75.8 kcal/mol
ΔG_f° (g)	67.1 kcal/mol
S° (g)	46.72 cal/degree mol
C_p (g)	4.97 cal/degree mol
ΔH_{fus}	4.757 kcal/mol
Coeff. linear expansion	9.2x10 ⁻⁶ /°C (at 25°C)

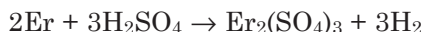
Production

Erbium metal is produced from rare-earth minerals. Methods of preparation are similar to dysprosium, involving sulfuric acid treatment, ion exchange separation from other lanthanides, roasting, conversion to halide, and finally high temperature reduction with calcium or sodium. (see Dysprosium).

Reactions

In aqueous solution, erbium is always trivalent, Er^{3+} . It forms water-insoluble trivalent salts, such as fluoride, ErF_3 , carbonate, $\text{Er}_2(\text{CO}_3)_2$, hydroxide, $\text{Er}(\text{OH})_3$, phosphate, ErPO_4 , and oxalate $\text{Er}_2(\text{C}_2\text{O}_4)_3$. It also forms water-soluble salts, chloride, ErCl_3 ; bromide, ErBr_3 ; iodide, ErI_3 ; sulfate, $\text{Er}_2(\text{SO}_4)_3$; and nitrate, $\text{Er}(\text{NO}_3)_3$. Evaporation of solutions generally yields hydrated salts.

The metal reacts with acids, forming corresponding salts and liberating hydrogen:



When heated in oxygen or air, the metal (in lump form) slowly oxidizes forming erbium sesquioxide, Er_2O_3 .

Analysis

Erbium may be analyzed by atomic absorption or emission spectrophotometry. Other instrumental analyses involve ICP-MS and x-ray techniques.

EUROPIUM

[7440-53-1]

Symbol: Eu; atomic number 63; atomic weight 151.97; a lanthanide group inner transition metal; electron configuration $[\text{Xe}]4f^65d^16s^2$ (partially filled orbitals); valence states +3 and +2.

History, Occurrence, and Uses

Boisbaudran obtained this rare earth element in 1892 in basic fractions from samarium-gadolinium concentrates, but it was not identified for several years. Demarcay obtained the element in the pure form in 1901. The element was named after Europe. It is found in nature mixed with other rare earth elements. Its concentration, however, is much lower than most other lanthanide elements. The principal rare earth ores are xenotime, monazite, and bastnaesite.

Europium is used for the capture of thermal neutrons for nuclear control rods in atomic power stations. Thermal neutron absorption of the natural mixture of europium isotopes is 4,600 barns. While its salts are used in coatings for cathode ray tubes in color televisions, organoderivatives are used in NMR spectroscopy.

Physical Properties

Soft silvery metal; body-centered cubic crystal lattice; density 5.24 g/cm³; melts at 822°C; vaporizes at 1,596°C; electrical resistivity 81 microhm-cm; reacts with water; soluble in liquid ammonia.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$S^\circ(\text{cry})$	18.6 cal/degree mol
$C_p(\text{cry})$	6.62 cal/degree mol
$\Delta H_f^\circ(\text{g})$	41.90 kcal/mol
$\Delta G_f^\circ(\text{g})$	33.99 kcal/mol
$S^\circ(\text{g})$	45.12 cal/degree mol
$C_p(\text{g})$	4.97 cal/degree mol
ΔH_{fus}	2.20 kcal/mol
Coeff. linear expansion	$32 \times 10^{-6}/^\circ\text{C}$

Preparation

Europium generally is produced from two common rare earth minerals: monazite, a rare earth-thorium orthophosphate, and bastnasite, a rare earth fluocarbonate. The ores are crushed and subjected to flotation. They are opened by sulfuric acid. Reaction with concentrated sulfuric acid at a temperature between 130 to 170°C converts thorium and the rare earths to their hydrous sulfates. The reaction is exothermic which raises the temperature to 250°C. The product sulfates are treated with cold water which dissolves the thorium and rare earth sulfates. The solution is then treated with sodium sulfate which precipitates rare earth elements by forming rare earth-sodium double salts. The precipitate is heated with sodium hydroxide to obtain rare earth hydrated oxides. Upon heating and drying, cerium hydrated oxide oxidizes to tetravalent ceric(IV) hydroxide. When the hydrated oxides are treated with hydrochloric acid or nitric acid, all but Ce^{4+} salt dissolves in the acid. The insoluble Ce^{4+} salt is removed.

Acid soluble rare earth salt solution after the removal of cerium may be subjected to ion exchange, fractional crystallization or solvent extraction processes to separate individual rare earths. Europium is obtained commercially from rare earths mixture by the McCoy process. Solution containing Eu^{3+} is treated with Zn in the presence of barium and sulfate ions. The trivalent europium is reduced to divalent state; whereby it coprecipitates as europium sulfate, EuSO_4 with isomorphous barium sulfate, BaSO_4 . Mixed europium(II) barium sulfate is treated with nitric acid or hydrogen peroxide to oxidize Eu(II) to Eu(III) salt which is soluble. This separates Eu^{3+} from barium. The process is repeated several times to concentrate and upgrade europium content to about 50% of the total rare earth oxides in the mixture. Treatment with concentrated hydrochloric acid precipitates europium(II) chloride dihydrate, $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ with a yield over 99%.

Several other processes also are applied for the commercial production of europium. In general, all processes are based upon the initial steps involving opening the mineral (bastnasite or monazite) with sulfuric acid or sodium hydroxide, often followed by roasting and solubilization. In one such process after separation of cerium, the soluble rare earth chloride mixture in HCl solution is pH adjusted and treated with bis(2-ethylhexyl)phosphate to obtain europium sesquioxide, Eu_2O_3 .

In the Bronaugh process, when the rare earth mixture contains europium in +2 oxidation state while all other lanthanide elements are in +3 state, the mixture is treated with ammonium hydroxide. While europium dissolves in the basic NH_4OH solution, all other metals precipitate as hydrous oxides (hydroxides). The filtrate containing europium is treated with oxalic acid. Europium oxalate formed is calcined to yield europium sesquioxide. High purity Eu_2O_3 may be separated from other rare earths on a cation exchange resin that is eluted with EDTA or other chelating agents.

Europium metal is prepared from the europium sesquioxide obtained above by the reduction with lanthanum or cerium. The oxide is heated under a vacuum in a tantalum crucible with excess lanthanum turning. Europium volatilizes and collects as a bright crystalline condensate on the wall of the crucible. It is stored and handled in an inert atmosphere, as the finely divided metal is flammable.

Analysis

Europium metal may be analyzed by AA, ICP and X-ray methods. The metal or its salts must be digested with nitric acid and brought into aqueous solution prior to analysis by flame or furnace AA or ICP spectrophotometry.

FERMIUM

[7440-72-4]

Symbol Fm; atomic number 100; atomic weight 257; a man-made transuranium radioactive element of the actinide series; electron configuration $[\text{Rn}]5f^{12}7s^2$; oxidation state +3; sixteen isotopes are known; most stable isotope Fm-257, $t_{1/2}$ 100.5 days.

The isotopes, their half-lives and decay modes are tabulated below:

<u>Isotopes</u>	<u>Half-lives</u>	<u>Decay Mode</u>
Fm-244	4.5 sec	Alpha decay
Fm-245	3.3 msec	Spontaneous fission
Fm-246	1.6 sec	Alpha decay
Fm-247	35 sec	Alpha decay
Fm-248	0.6 min	Alpha decay
Fm-249	2.5 min	Alpha decay
Fm-250	30 min	Alpha decay
Fm-251	7 hr	Orbital electron capture, Alpha decay
Fm-252	25 hr	Alpha decay, Spontaneous fission
Fm-253	3 days	Orbital electron capture, Alpha decay
Fm-254	3.24 hr	Alpha decay, Spontaneous fission
Fm-255	20 hr	Alpha decay, Spontaneous fission
Fm-256	2.7 hr	Alpha decay, Spontaneous fission
Fm-257	97 days	Alpha decay, Spontaneous fission

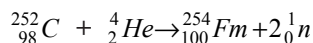
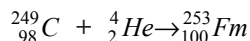
History

Fermium was formally discovered in 1954 at the Nobel Institute for Physics in Stockholm. It was synthesized in 1952 in the Material Testing Reactor in Idaho, but the discovery was not announced. The new element was named in honor of Enrico Fermi. There is no commercial application of this element because its yield is in extremely minute quantities. It has been detected in debris from thermonuclear explosion.

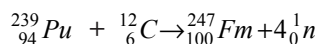
Production

Heavier isotopes such as Fm -254, -255, -256, and -257 can be produced in a nuclear reactor by multiple neutron capture reactions when heavy elements are subjected to intense neutron irradiation. Such reactions also occur in thermonuclear explosion.

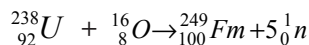
Isotopes of mass numbers from 250 to 254 have been prepared by alpha particle bombardments of californium -249 and -252:



Lighter isotopes such as Fm -247 and -248 were synthesized by bombarding plutonium -239 and -240, respectively, with carbon -12 ions:



Fermium -249 was obtained (during its synthesis in 1954) by bombarding uranium -238 with oxygen ions:



All these isotopes may also be synthesized by other nuclear processes.

Chemical Properties

The chemical properties of fermium are very similar to those of other trivalent actinide series elements, californium and einsteinium. The element's oxidation state +3 is its only known oxidation state.

FLUORINE

[7782-41-4]

Symbol: F; atomic number 9; atomic weight 37.997; a Group VIIA (Group 17) nonmetallic element; first member of halogen group elements; electron configuration [He]2s²2p⁵; valence -1; electronegativity 4.0; electron affinity 79.5 kcal/g-atom

History, Occurrence, and Uses

The element was identified by Davy in 1813 and named fluorine by Ampere. However, it was prepared successfully first in elemental form by Moissan in 1886. Fluorine is distributed widely in nature and occurs in several minerals. The most common minerals are fluorspar, CaF_2 ; cryolite, $3\text{NaF} \cdot \text{AlF}_3$; and fluorapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$. Its concentration in the earth's crust is 585 mg/kg, and is 1.3 mg/kg in sea water.

Fluorine is used in the separation of uranium, neptunium and plutonium isotopes by converting them into hexafluorides followed by gaseous diffusion; then recovering these elements from nuclear reactors. It is used also as an oxidizer in rocket-fuel mixtures. Other applications are production of many fluoro compounds of commercial importance, such as sulfur hexafluoride, chlorine trifluoride and various fluorocarbons.

Physical Properties

Pale yellow gas; occurs as a diatomic gas at ordinary temperatures and pressures; density (of liquid fluorine) at -188°C is 1.108 g/mL; density of the gas at 0°C is 1.696 g/L; liquefies at -188.12°C ; solidifies at -219.66°C ; critical temperature -129.02°C , critical pressure 51.04 atm; critical volume 66 cm^3/mol ; reacts with water.

Thermochemical Properties

$\Delta H_f^\circ (\text{F})$	-18.88 kcal/mol
$\Delta G_f^\circ (\text{F})$	-14.80 kcal/mol
$S^\circ (\text{F})$	37.9 cal/degree mol
$C_p (\text{F})$	5.44 cal/degree mol
$\Delta H_f^\circ (\text{F}_2)$	0.0
$\Delta G_f^\circ (\text{F}_2)$	0.0
$S^\circ (\text{F}_2)$	48.44 cal/degree mol
$C_p (\text{F}_2)$	7.48 cal/degree mol
ΔH_{vap}	1.582 kcal/mol
ΔH_{fus}	0.122 kcal/mol
ΔH_{dissoc}	37.7 kcal/mol

Preparation

Fluorine is manufactured commercially by an electrolysis process which has not changed much since Moissan first isolated it. The electrolytes consist of an aqueous mixture of potassium fluoride and hydrogen fluoride, HF solution, the molar ratio of KF to HF usually being 1:1 or 2:1. Electrolysis of hydrogen fluoride produces fluorine gas at the ungraphitized carbon anode and hydrogen gas at the mild steel cathode. Potassium fluoride makes the solution electrically conductive (pure HF is a nonconductor). In many commercial processes, a KF to HF molar ratio of 2:1 is used. At this composition, the partial pressure of HF over the electrolyte is low, and the temperature of the melt is 70° . However, fluorine produced by this process usually contains about 5 to 10% hydrogen fluoride. HF can be removed by passing fluorine-HF mixture over dry sodium fluoride. HF is retained over sodium fluoride, thus

purifying fluorine gas to over 99%.

Fluorine gas is sold commercially in stainless steel or monel cylinders as compressed gas or as liquid fluorine.

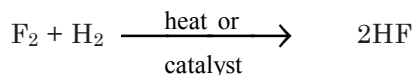
Reactions

Fluorine is the most electronegative element in the Periodic Table. It also is the most reactive nonmetal, and the most powerful oxidizing agent:

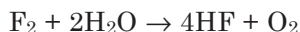


It combines with practically all elements (except helium, neon, and nitrogen) and most compounds. It combines with oxygen at elevated temperatures in an electric furnace. Its compounds with inert gases xenon, argon, krypton, and radon are known.

Fluorine reacts with gaseous hydrogen forming hydrogen fluoride. Although the reaction is highly exothermic ($\Delta H_{\text{rxn}} = -64 \text{ kcal/mol}$), it requires high temperature or a catalyst for initiation:



Reaction with water is complex, producing hydrofluoric acid and oxygen as the main products:



Minor products such as hydrogen peroxide (H_2O_2), oxygen difluoride (OF_2), and ozone (O_3), may form in small yields depending on conditions of the reactions.

Nonmetals, such as sulfur, phosphorus and carbon (amorphous) inflame in fluorine forming their corresponding fluoro compounds, such as sulfur hexafluoride (SF_6), phosphorus pentafluoride (PF_5), and carbon tetrafluoride (CF_4).

Fluorine also reacts with other halogens, forming interhalogen compounds. While with bromine and iodine it reacts vigorously at ordinary temperatures, with chlorine the reaction occurs at 200°C . Such interhalogen products with these halogens include iodine heptafluoride, bromine trifluoride, bromine pentafluoride, and chlorine trifluoride. Metalloid elements, such as arsenic, silicon, selenium, and boron also inflame in a stream of fluorine, forming fluorides.

All metals react with fluorine to form metal fluorides. With alkali metals the reactions are violent and highly exothermic at ordinary temperatures. Other metals react at high temperatures. Many metals in their solid form react with fluorine at ordinary temperatures, forming protective coatings of metal fluorides which prevent any further fluoride formation. Such metals include copper, nickel and aluminum, which mostly are metals of construction. Protective coatings of these metal fluorides have very low volatility, thus preventing further fluorination. However, with certain metals such as titani-

um, tungsten, and vanadium, such protective fluoride coatings can volatilize readily at high temperatures, allowing the metals to burn vigorously in fluorine.

Reaction of fluorine with an aqueous alkali solution is complex and depends on reaction conditions. A major product of such reaction is oxygen difluoride, OF₂. In cold alkali solution, the products constitute metal fluoride, oxygen difluoride, water, and oxygen:



Fluorine reacts with sulfuric acid to yield fluorosulfuric acid, HFSO₃, and with nitric acid it forms fluorine nitrate, NO₃F, an explosive gas.

Fluorine reacts with hydrocarbons in vapor phase, producing fluorocarbon compounds in which hydrogen atoms are substituted with fluorine atoms. The strong C—F bond with bond energy in the order of 110 kcal/mol imparts greater stability to such fluorocarbon derivatives in which the fluorine atoms(s) also shield the carbon skeleton from chemical attack. The fluorination of hydrocarbons is, however, more conveniently carried out using hydrogen fluoride, ammonium fluoride, reactive metal fluorides, or by electrolytic fluorination than by using elemental fluorine, with which the reaction is difficult to control.

Analysis

Analysis may be performed by reacting the gas in water (or allowing the contaminated air to bubble through water) and determining the fluoride ion in the solution using a fluoride ion selective electrode, or analyzing the solution by ion chromatography. Solution may require appropriate dilutions prior to measurements. Air may be sampled in a stainless steel or monel canister by repeated evacuation and filling and the contents transported by helium onto a cryogenically cooled GC port. The mixture is separated on a suitable temperature programmed column and measured by a halogen specific detector or by a mass selective detector. The characteristic mass ion for the element is 19. Alternatively, fluorine may be converted into fluorosilicic acid, H₂SiF₆ which may be precipitated either as calcium fluoride or measured by titration with a standard solution of thorium nitrate.

Hazard

Because of its high reactivity, many fluorine reactions are violent and may cause explosion if not carried out under controlled conditions. Reactions with hydrogen, acetylene, ammonia, chlorine dioxide, sulfur dioxide, and a number of organics can be explosive. Also, it forms shock-sensitive products with a number of compounds including perchloric acid, nitric acid, alkali metal nitrates and nitrites, azides and sodium acetate (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., pp. 439-40. New York: Wiley Interscience). Reaction with water is violent even at low temperatures. A large number of inorganic and organic substances ignite in fluorine atmosphere.

Fluorine gas is a severe irritant to eyes, skin, and mucous membranes. Acute exposure can cause respiratory tract irritation and pulmonary edema. Chronic exposure can cause mottling of teeth and injury to lungs, liver and kidney.

FLUORINE NITRATE

[7789-26-6]

Formula: FNO_3 ; MW 81.003

Synonyms: nitrogen trioxyfluoride; nitroxy fluoride; nitryl hypofluorite.

Uses

Fluorine nitrate is used in rocket propellants as an oxidizing agent.

Physical Properties

Colorless gas; acrid odor; density 3.554 g/L at 25°C; liquefies at -46°C; density of liquid 1.507 g/mL at -46°C; solidifies at -175°C; reacts with water (forming HF, OF_2 , HNO_3 and O_2); also reacts with ethanol, ether and aniline; soluble in acetone.

Thermochemical Properties

$$\Delta H_f^\circ \quad 2.486 \text{ kcal/mol}$$

Preparation

Fluorine nitrate may be prepared by the action of fluorine on nitric acid:



Also, it is produced when nitrogeous compounds are electrolyzed in hydrofluoric acid.

Hazard

Fluorine nitrate is shock sensitive, especially in liquid state. The liquefied material explodes when shaken vigorously or in contact with alcohol, ether, aniline, or grease (Bretherick's *Handbook of Reactive Chemical Hazards*, 5th. Ed., P. Urben (ed.) 1995, pp 1405-6, Oxford, UK: Butterworth-Heinemann). The gas catches fire when mixed with ammonia or hydrogen sulfide.

FRANCIUM

[7440-73-5]

Symbol Fr; atomic number 87; atomic weight 223; heaviest alkali metal element of Group IA (Group 1); a radioactive element; electron configuration $[\text{Rn}]7s^1$; oxidation state +1; the most electropositive element; the most stable isotope, Fr-223 ($t_{1/2}$ 21 minutes), also is the only natural isotope. Isotopes, half-lives and their decay modes are shown below:

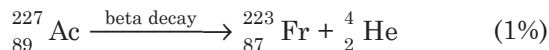
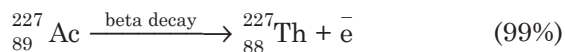
<u>Isotopes</u>	<u>Half-lives</u>	<u>Decay mode</u>
Fr-203	0.7 sec	Alpha emission
Fr-204	3.3 sec	Alpha emission
Fr-204 (isomer)	2.2 sec	Alpha emission
Fr-205	3.7 sec	Alpha emission
Fr-206	16 sec	Alpha emission
Fr-207	15 sec	Alpha emission
Fr-208	60 sec	Alpha emission
Fr-209	52 sec	Alpha emission
Fr-210	3.2 min	Alpha emission
Fr-211	3.0 min	Alpha emission
Fr-212	19 min	Alpha emission
Fr-213	34 sec	Alpha emission
Fr-218	0.005 sec	Alpha emission
Fr-219	0.02 sec	Alpha emission
Fr-220	27.5 sec	Alpha emission
Fr-221	4.8 min	Alpha emission
Fr-222	15 min	Beta decay
Fr-223	21 min	Beta decay (99%), Alpha decay (0.005%)
Fr-224	2 min	Beta decay

History and Occurrence

Francium occurs in decay products of actinium. It was discovered by French physicist Marguerite Perey in 1939 and named after France. No weighable amount ever has been prepared.

Preparation

Francium-223 is produced from the decay of actinium-227. While the chief decay product is thorium-227 resulting from beta emission, actinium-227 also undergoes alpha emission to an extent of one percent giving francium-223:



GADOLINIUM

[7440-54-2]

Symbol Gd; atomic number 64; atomic weight 157.25; a lanthanide series rare earth element; electron configuration $4f^7 5d^1 6s^2$; partially filled *f* orbital; common oxidation state +3; six stable natural isotopes: Gd-152 (0.2%), Gd-154 (2.86%), Gd-155 (15.61%), Gd-156 (20.59%), Gd-157 (16.42%), Gd-157 (23.45%)

History, Occurrence, and Uses

Gadolinium is found in minerals bastnasite and monazite, always associated with other rare earth metals. It was isolated from yttria in 1880 by the Swiss chemist Marignac, and discovered independently in 1885 by Boisbaudran. It was named in honor of the Swedish chemist Gadolin. Its abundance in the earth's crust is 6.2 mg/kg and concentration in sea water is 0.7 ng/L.

The most important application of this metal is as control rod material for shielding in nuclear power reactors. Its thermal neutron absorption cross section is 46,000 barns. Other uses are in thermoelectric generating devices, as a thermoionic emitter, in yttrium-iron garnets in microwave filters to detect low intensity signals, as an activator in many phosphors, for deoxidation of molten titanium, and as a catalyst. Catalytic applications include decarboxylation of oxaloacetic acid; conversion of *ortho*- to *para*-hydrogen; and polymerization of ethylene.

Physical Properties

Colorless or light yellow metal; at ordinary temperatures it occurs in hexagonal close-packed crystalline form, known as alpha-gadolinium; alpha form transforms to a body-centered cubic allotropic form, beta-gadolinium upon heating at 1,262°C; density 7.90 g/cm³; melting point 1,313°C; vaporizes at 3,266°C; vapor pressure 9.0 torr at 1,800°C (calculated); electrical resistivity 134.0 microhm-cm at 25°C; Poisson ratio 0.259; modulus of elasticity 8.15x10⁶ psi; thermal neutron absorption cross section 46,000 barns; insoluble in water; dissolves in acid (reacts).

Thermochemical Properties

ΔH_f°	0.0
ΔG_f°	0.0
S°	16.27 cal/degree mol
C_p	8.85 cal/degree mol
ΔH_{fus}	2.34 kcal/mol
ΔH_{vap}	72.0 kcal/mol
Coeff. linear expansion	$8.6 \times 10^{-6}/^\circ\text{C}$

Production

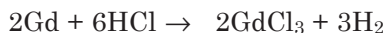
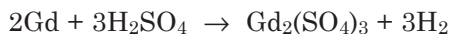
Gadolinium is produced from both its ores, monazite and bastnasite. After the initial steps of crushing and beneficiation, rare earths in the form of oxides are attacked by sulfuric or hydrochloric acid. Insoluble rare earth oxides are converted into soluble sulfates or chlorides. When produced from monazite sand, the mixture of sand and sulfuric acid is initially heated at 150°C in cast iron vessels. Exothermic reaction sustains the temperature at about 200 to 250°C. The reaction mixture is cooled and treated with cold water to dissolve rare earth sulfates. The solution is then treated with sodium pyrophosphate to precipitate thorium. Cerium is removed next. Treatment with caustic soda solution followed by air drying converts the metal to cerium(IV) hydroxide. Treatment with hydrochloric or nitric acid sol-

utilizes all rare earths except cerium. Rare earth salt solution is then treated with magnesium nitrate. The double salts of samarium, europium, and gadolinium nitrate crystallize out. Individual salts are separated by ion exchange methods.

Gadolinium is obtained from its salts, usually its chloride or fluoride, by heating with excess calcium at 1,450°C under argon. The reduction is carried out in a tantalum crucible. Alternatively, fused gadolinium chloride mixed with sodium or potassium chloride is electrolyzed in an iron pot that serves as the anode and using a graphite cathode. Sponge gadolinium may be produced by reducing molten gadolinium chloride with a reducing metal oxide in vaporized state at a temperature below 1,300°C (the melting point of gadolinium) at a reduced pressure.

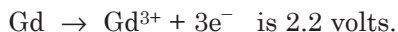
Reactions

The only oxidation state known for this metal is +3. Therefore, all its compounds are trivalent. It reacts with dilute mineral acids forming the corresponding salts. The reaction is vigorous but usually not violent.

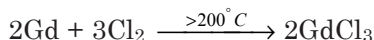


Although the metal is stable in air at ordinary temperature, it burns in air when heated at 150 to 180°C, particularly when present in sponge or powdered form having a large surface area. The product is gadolinium(III) oxide, Gd_2O_3 .

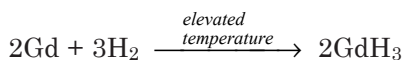
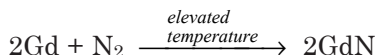
Gadolinium is a strong reducing agent. It reduces oxides of several metals such as iron, chromium, lead, manganese, tin, and zirconium into their elements. The standard oxidation potential for the reaction



Gadolinium burns in halogen vapors above 200°C forming gadolinium(III) halides:



When heated with sulfur, the product is gadolinium sulfide Gd_2S_3 . Similarly, at elevated temperatures, gadolinium combines with other non-metals such as nitrogen, hydrogen, and carbon forming nitride, hydride, and carbide respectively:



Analysis

Gadolinium may be measured in an acidic solution by flame or furnace atomic absorption or ICP atomic emission spectrophotometry. Also, gadolinium may be identified nondestructively and rapidly by x-ray fluorescence methods. It also may be measured by neutron activation analysis, and by various spectrophotometric techniques. The element shows sharp absorption bands in ultraviolet region at 270–280 nm. Other lanthanides also produce bands in this region; however, those are low intensity minor bands.

GADOLINIUM(III) CHLORIDE

[10138-52-0]

Formula: GdCl_3 ; MW 263.61; forms a hexahydrate, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ [19423–81–5]

Uses

GdCl_3 is used for preparing gadolinium metal.

Physical Properties

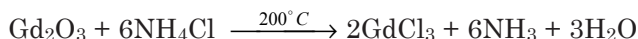
White monoclinic crystal; hygroscopic; density 4.52 g/cm³; melts at 609°C; soluble in water.

Thermochemical Properties

ΔH_f°	–240.9 kcal/degree mol
C_p	21.0 cal/degree mol

Preparation

GdCl_3 is prepared by heating gadolinium(III) oxide with excess of ammonium chloride above 200°C:

**Analysis**

Elemental composition: Gd 59.65%, Cl 41.35%. GdCl_3 aqueous solution is analyzed for Gd metal by AA or ICP spectrometry, and for chloride ion by ion chromatography, chloride ion selective electrode, or titration with silver nitrate using potassium chromate indicator.

GADOLINIUM(III) OXIDE

[12064-62-9]

Formula: Gd_2O_3 ; MW 362.50

Synonym: gadolinia

Uses

Gadolinium oxide is used in control rods for neutron shielding in nuclear power reactors. It also is used in filament coatings, ceramics, special glasses and TV phosphor activator. The compound also is used as a catalyst.

Physical Properties

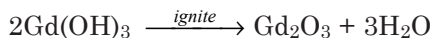
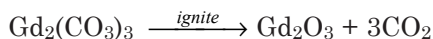
White powder; hygroscopic; density 7.07 g/cm³; melts at 2,420°C; insoluble in water ($K_{sp}=1.8 \times 10^{-23}$); soluble in acid.

Thermochemical Properties

ΔH_f°	-434.9 kcal/degree mol
C_p	25.5 cal/degree mol

Preparation

Gadolinium oxide is prepared by calcinations of gadolinium carbonate, -hydroxide, -nitrate, or -oxalate:

**Analysis**

Elemental composition: Gd 86.76%, O 13.24%. A weighted amount of compound is dissolved in nitric acid, diluted, and analyzed by AA or ICP technique. The solid powder may be characterized nondestructively by x-ray methods.

GADOLINIUM(III) SULFATE OCTAHYDRATE

[13450-87-8]

Formula: $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$; MW 746.81

Uses

$\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is used in cryogenic work; and in thermoelectric devices

Physical Properties

Colorless monoclinic crystals; density 3.01/cm³ (at 15°C); loses water of crystallization at 400°C; density of anhydrous salt 4.14 g/cm³; decomposes at 500°C; soluble in cold water; solubility decreases with rise in temperature.

Preparation

The hydrated sulfate is obtained by dissolving gadolinium(III) oxide in

dilute sulfuric acid followed by crystallization:



Analysis

Elemental composition: Gd 42.11%, S 12.88%, H 2.16%, O 42.85%. An aqueous solution of weighted amount of salt is analyzed for gadolinium by AA or ICP spectrometry and sulfate anion by ion chromatography. The water of hydration may be measured by gravimetry, heating a weighted amount of salt at 400°C to expel the water followed by cooling and weighing.

GALLIUM

[7440-55-3]

Symbol Ga; atomic number 31; atomic weight 69.723; a Group IIIA (Group 13) element; electron configuration $[\text{Ar}]3\text{d}^{10}4\text{s}^24\text{p}^1$; oxidation state +3, also exhibits +2 and +1; ionic radius, Ga^{3+} 1.13Å; two stable natural isotopes: Ga-69 (60.20%), Ga-71 (39.80%).

History, Occurrence, and Uses

The existence of this element was predicted by Mendeleev as a missing link between aluminum and indium during his periodic classification of elements. Mendeleev termed it ekaaluminum. The element was discovered in 1875 by French chemist Lecoq de Boisbaudran while he was carrying out spectroscopic examination of emission lines from Pyrenean zinc blende concentrates. Boisbaudran named this new element gallium, after Gallia, the Latin word for his native France. In the same year, Boisbaudran also separated gallium by electrolysis.

Gallium is widely distributed in nature, mostly found in trace amounts in many minerals including sphalerite, diaspore, bauxite, and germanite. It is found in all aluminum ores. Gallium sulfide occurs in several zinc and germanium ores in trace amounts. It also is often found in flue dusts from burning coal. Abundance of this element in the earth's crust is about 19 mg/kg. Its average concentration in sea water is 30 ng/L.

The most important use of gallium is as a doping agent for semiconductors, transistors, and other solid state devices. It is used to produce semiconducting compounds. Miscellaneous important semiconductor applications include magnetic field sensing, temperature sensing, and voltage amplification. Some gallium compounds, such as gallium arsenide, gallium phosphide, and magnesium gallate have major applications in electroluminescent light emission, microwave generation, and UV activated powder phosphors. Another important use of gallium in oxide form involves spectroscopic analysis of uranium oxide. Gallium also is used to make many low melting alloys. Some other uses for gallium are in high-temperature thermometers as a thermometric fluid; in high vacuum systems as a liquid sealant; as a heat-transfer medium; and to produce mirrors on glass surfaces.

Physical Properties

Gray orthogonal crystal or silvery liquid; the ultrapure material has silver-like appearance; density of solid 5.904 g/cm³ at 29.6°C; specific gravity of liquid 6.095 at 29.6°C; melts near room temperature at 29.6°C; supercools below its freezing point (seeding may be required for solidification); expands on solidification (3.1%); vaporizes at 2,204°C; exists in liquid state in the widest temperature range (i.e., among all elements gallium occurs as liquid in the widest range of temperature); vapor pressure 0.0001 torr at 900°C (lowest vapor pressure for any element in liquid state at this temperature), 0.0008 torr at 1,000°C, 1 torr at 1,350°C, and 5 torr at 1,478°C; surface tension 735 dynes/cm at 30°C; viscosity 1.60 and 0.81 centipoise at 100°C and 500°C, respectively.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (liq)	1.34 kcal/mol
S° (cry)	9.78 cal/degree mol
C_p (cry)	6.19 cal/degree mol
H_{vap}	60.71 kcal/mol
Thermal conductivity (30°C)	0.08 cal/sec/cm/°C
Coeff. linear expansion	$18 \times 10^{-6}/^\circ\text{C}$

Production

All gallium minerals contain the element only in very small amounts. It is, therefore, obtained as a by-product during production of aluminum or zinc.

Gallium occurs as a hydrated oxide (hydroxide) in all aluminum minerals including bauxite, clay, and laterite. The ore is digested with a hot solution of caustic soda (Bayer process). This converts aluminum to sodium aluminate and the small quantities of gallium that are present in the ore into sodium gallate. On cooling and seeding the liquor most aluminum salt precipitates along with small quantities of gallium as coprecipitate. After aluminum separates, the supernatant solution becomes richer in gallium. Its concentration even at this stage is not adequate for electrolytic recovery from the solution.

Also, supernatant solution in the Bayer liquor still contains an appreciable amount of soluble aluminum salt that needs to be removed by electrolysis prior to gallium recovery. This may be done either by treating the solution with lime to precipitate out calcium aluminate or by neutralizing the solution with carbon dioxide to precipitate alumina hydrate (Hudson, L.K. 1965. *J. Metals*, 17, pp. 948-51). Removal of most aluminum by these processes enhances the concentration of gallium in the solution to a level of approximately 0.1% whereupon the solution may be electrolyzed using an anode, cathode, and cell made of stainless steel.

Gallium may be recovered from zinc sulfide ores by a series of steps that include oxidation, acid treatments, neutralization, precipitation, alkali treatment, and electrolysis (Foster, L.M. 1968. Gallium. In the *Encyclopedia of Chemical Elements*, ed. C. L. Hampel. pp. 231-237, New York: Reinhold Publishing Corp.). The process is described below.

The sulfide ore is roasted in air to convert it into oxide. The oxide is treated with sulfuric acid. The acid solution now contains zinc sulfate along with sulfates of aluminum, iron, gallium, and other impurity metals. Upon neutralization, iron and aluminum precipitate out along with gallium. The "iron mud" so obtained is treated with caustic soda solution to solubilize gallium and aluminum. Neutralization of this solution yields precipitates of hydrated oxides of aluminum and gallium. The precipitate is dissolved in hydrochloric acid to form gallium chloride and some aluminum chloride. Gallium chloride is highly soluble in ether and, therefore may be separated from the acid solution by ether extraction. The ether extract is treated with caustic soda solution to precipitate out remaining iron impurities. The alkaline solution containing gallium is electrolyzed to recover the element.

The crude material may be purified by acid wash and fractional crystallization to obtain 99.999% gallium for its semiconductor applications. Gallium is one of the purest elements that may be produced commercially. It is transported in molten state. The element supercools below its normal freezing point. To initiate solidification, molten gallium is 'seeded' with a solid crystal. A small crystal of appropriate orientation in any desired crystallographic axis is brought in contact with the surface of supercooled liquid through a thin layer of dilute hydrochloric acid. The acid removes the thin solid oxide film from the surface. Solidification begins when the seed touches the surface of supercooled liquid gallium, and the crystallographic orientation of the seed is maintained throughout the process.

Chemical Reactions

Chemical properties of gallium fall between those of aluminum and indium. It forms mostly the binary and oxo compounds in +3 oxidation state. It forms a stable oxide, Ga_2O_3 and a relatively volatile suboxide, Ga_2O .

Gallium combines with halogens forming the halides, GaX_3 . Similarly, it combines with phosphorus, arsenic and antimony forming the corresponding binary compounds, which exhibit interesting semiconductor properties. With sulfur it forms sulfide. No reaction occurs with bismuth, although Ga dissolves in it. Reaction with nitrogen occurs at high temperatures forming gallium nitride, GaN , which is relatively unstable (decomposes above 600°C). Unlike aluminum, gallium does not form any carbide. Reactions with mineral acids are slow on high purity gallium.

Some lower valence compounds of gallium also are known. These include gallium suboxide, Ga_2O ; gallium sulfide, GaS ; gallium selenide, GaSe ; gallium telluride, GaTe ; gallium dichloride, GaCl_2 ; and gallium monochloride, GaCl . The monochloride exists only in vapor state.

Analysis

Gallium may be identified by its physical properties. Its compounds or elemental form may be analyzed by acid digestion followed by dilution of the acid and measurement at ppm to ppb range by atomic absorption, atomic emission, or x-ray fluorescence methods. It also may be identified by neutron activation analysis and ICP-MS techniques.

GALLIUM(III) ARSENIDE

[1303-00-0]

Formula: GaAs; MW 144.64

Uses

Gallium arsenide exhibits semiconductor properties. It is used in transistors, lasers, solar cells and various high-speed microcircuits.

Physical Properties

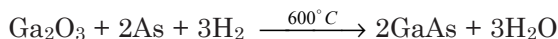
Gray cubic crystal; density 5.316 g/cm³; melts at 1,227°C; hardness 4.5 Mohs; lattice constant 5.653Å; dielectric constant 11.1; resistivity (intrinsic) at 27°C, 3.7×10⁸ ohm-cm.

Thermochemical Properties

ΔH_f°	-16.97 kcal/mol
ΔG_f°	-16.20 kcal/mol
S°	15.34 cal/degree mol
C_p	11.04 cal/degree mol
Coeff. linear expansion	$5.9 \times 10^{-6}/^\circ\text{C}$
Thermal conductivity	$0.52 \text{ Wcm}^{-1}\text{K}^{-1}$

Preparation

Gallium arsenide is prepared by passing a mixture of arsenic vapor and hydrogen over gallium(III) oxide heated at 600°C:



The molten material attacks quartz. Therefore, quartz boats coated with carbon by pyrolytic decomposition of methane should be used in refining the compound to obtain high purity material.

Gallium arsenide is produced in polycrystalline form as high purity, single crystals for electronic applications. It is produced as ingots or alloys, combined with indium arsenide or gallium phosphide, for semiconductor applications.

Analysis

Elemental composition: Ga 48.20%, As 51.80%. Both As and Ga may be analyzed by various instrumental techniques including flame and furnace AA, ICP spectrometry, and x-ray methods. A weighed amount of solid material is digested with nitric acid, diluted in water and analyzed for these metals. The crystals may be characterized nondestructively by their optical and electronic properties.

GALLIUM(III) CHLORIDE

[14350-90-3]

Formula: GaCl₃; MW 176.08**Uses**

Gallium(III) chloride is used to prepare other gallium salts and in solvent extraction. The chloride is highly soluble in solvent ether. This high solubility of metal chloride in ether allows metal extraction from ore.

Physical Properties

Colorless needles or glassy solids; density 2.47 g/cm³; melts at 77.9°C; vaporizes at 201°C; critical temperature 420.8°C; critical volume 263 cm³/mol.

Thermochemical Properties

ΔH_f°	-125.40 kcal/mol
ΔG_f°	-108.70 kcal/mol
S°	33.94 cal/degree mol
ΔH_{fus}	2.61 kcal/mol
ΔH_{vap}	5.71 kcal/mol

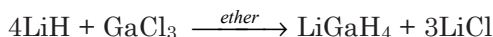
Preparation

Gallium(III) chloride is prepared by the reaction of gallium with hydrogen chloride. Also, it can be made by direct combination of gallium and chlorine. The reaction is highly vigorous.

Reactions

Reaction with ammonia or caustic soda solution yields a gelatinous precipitate of gallium hydroxide, Ga(OH)₃. Reaction of gallium(III) chloride with metallic gallium yields a solid dimeric dichloride, Ga₂Cl₄, having the structure Ga^I[Ga^{III}Cl₄]. In the presence of a donor ligand L, molecular adducts of structures Ga^{II}Cl₄•2L are formed. In these adducts, gallium exists in the oxidation state +2.

Reaction with lithium hydride in ether produces lithium gallium hydride:



The corresponding sodium salt has not been synthesized.

Gallium(III) chloride also combines with other metal chlorides such as CaCl₂ or CrCl₃ to form mixed chlorides that have halogen bridge structures; i.e., Cl₄Ta(-Cl)₂. Many such compounds are volatile.

Analysis

Elemental composition: Ga 39.60%, Cl 60.40%. The compound may be characterized by physical properties, electron diffraction and x-ray methods.

Gallium may be measured in aqueous solution by various instrumental methods (See Gallium), and chloride by ion chromatography.

GALLIUM PHOSPHIDE

[12063-98-8]

Formula: GaP; MW 100.70

Uses

Gallium phosphide is used in making semiconductors.

Physical Properties

Pale orange to yellow transparent cubic crystals or long whiskers; lattice constant 5.450Å; density 4.138 g/cm³; melts at 1,477°C; dielectric constant 8.4; electroluminescent in visible light.

Preparation

The compound is prepared by vapor phase reaction of gallium suboxide, Ga₂O and phosphorus. It is produced in polycrystalline form or as single crystals or whiskers in high purity grade for use in semiconducting devices.

Analysis

Elemental composition: Ga 69.24%, P 30.76%. Gallium phosphide may be characterized by its physical and electronic properties. It may also be analyzed by various x-ray methods. Gallium may be measured by AA and ICP spectrophotometry following digestion with nitric acid or aqua regia and appropriate dilution (See Gallium).

GALLIUM SESQUIOXIDE

[12024-21-4]

Formula: Ga₂O₃; MW 187.44

Synonyms: gallium(III) oxide; gallia

Uses

The compound is used in spectroscopic analysis and in preparing gallium arsenide for making semiconductors.

Physical Properties

White crystals; exists in three crystalline modifications: alpha-, beta-, and gamma-Ga₂O₃; while the alpha-form is analogous to the corundum form of alumina, the beta-Ga₂O₃ is isomorphous with theta-alumina; alpha-form converts to beta-modification on calcination at high temperatures (600°C); gamma form is stable at low temperatures; density 6.44 g/cm³ (alpha-Ga₂O₃),

5.88 g/cm³ (beta- Ga₂O₃); melts at 1,725°C; soluble in most acids.

Thermochemical Properties

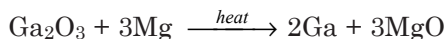
ΔH_f°	-260.3 kcal/mol
ΔG_f°	-238.6 kcal/mol
S°	20.32 cal/degree mol
C_p	22.01 cal/degree mol

Preparation

Gallium sesquioxide is precipitated in hydrated form upon neutralization of acidic or basic solution of gallium salt. Also, it is prepared by thermal decomposition of gallium salts. Gallium oxide hydroxide, GaOOH [20665-52-5] on calcinations at high temperatures yields beta- Ga₂O₃.

Reactions

Gallium sesquioxide is reduced to gallium suboxide, Ga₂O [12024-20-3] by common reducing agents. Also, heating the sesquioxide with gallium metal yields gallium suboxide. Heating with magnesium reduces the oxide to elemental form in a violent reaction:



Heating with mineral acids yields corresponding gallium salts. When heated with a mixture of hydrogen and arsenic vapors at 600°C, gallium arsenide, GaAs is produced. When heated with alkali metal oxide at 1,000°C, alkali metal gallates, such as K₂Ga₂O₆ are formed.

Analysis

Elemental composition: Ga 74.39%, O 25.61%. The compound may be characterized by x-ray methods. Gallium may be analyzed in a diluted acid extract by AA or ICP spectrophotometry (see Gallium).

GERMANIUM

[7440-56-4]

Symbol Ge; atomic number 32; atomic weight 72.61; a Group IVA (Group 14) metalloid element; electron configuration [Ar]3d¹⁰4s²4p²; oxidation states +2 and +4; electronegativity 1.9; covalent radius (tetrahedral, sp³) 1.22Å; ionic radius: Ge²⁺ 0.93Å, Ge⁴⁺ 0.53Å; isotopes and their natural abundance: Ge-70 (20.15%), Ge-72 (27.43%), Ge-73 (7.76%), Ge-74 (36.54%), Ge-76 (7.76%).

History, Occurrence, and Uses

The existence of this element was predicted by Mendeleev in 1871 in his periodic scheme. He predicted that it should belong to the carbon group and occupy the position just below silicon. He therefore named it ekasilicon.

Fifteen years later in 1886, the predicted element was discovered by Clemens Winkler who isolated it from the mineral argyrodite. It was named in honor of Germany.

Germanium occurs in nature mostly as sulfide ores. It is found in the minerals germanite, $7\text{CuS} \cdot \text{FeS} \cdot \text{GeS}_2$; argyrodite, $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$; renierite $(\text{Cu}, \text{Ge}, \text{Fe}, \text{Zn}, \text{As})\text{S}$; and canfieldite, $4\text{Ag}_2\text{S}$. It also is found in small quantities in many zinc blende ores from which it is commercially extracted in the United States. Trace quantities of germanium are also found in many coals. Its abundance in the earth's crust is about 1.5 mg/kg and concentration in sea water is 0.05 $\mu\text{g/L}$.

The most important uses of germanium are in electronic industries. It is a semiconductor material exhibiting an exponential increase of conductivity with increasing temperature. The element can be prepared in extreme purification with a high degree of crystalline perfection so as to yield highly characterized surfaces. Other applications of germanium are in infrared detectors, microscopes and various optical instruments; as a phosphor in fluorescent lamps; as an alloying agent; and as a catalyst.

Physical Properties

Grayish-white cubic crystals; lustrous and brittle; density 5.323 g/cm^3 ; hardness 6.0 Mohs; melts at 938.2°C; vaporizes at 2,833°C; a poor conductor of electricity; electrical resistivity 47 microhm-cm; dielectric constant 15.7; specific magnetic susceptibility (at 20°C) 0.122×10^{-6} ; insoluble in water, dilute acids and dilute alkalies; attacked by concentrated nitric and sulfuric acids, aqua regia and fused alkalies.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (g)	88.9 kcal/mol
ΔG_f° (g)	79.2 kcal/mol
S° (cry)	7.43 cal/degree mol
S° (g)	40.1 cal/degree mol
C_p (cry)	5.57 cal/degree mol
C_p (g)	7.38 cal/degree mol
ΔH_{fus}	8.83 kcal/mol
ΔH_{vap}	79.8 kcal/mol
Thermal conductivity (at 25°C)	0.14 cal/sec/cm/°C
Coeff. linear expansion (at 25°C)	$6.1 \times 10^{-6}/^\circ\text{C}$

Production

In the United States, germanium is obtained as a by-product of zinc production from zinc blende ores. The ore is concentrated by the flotation process. Concentrated ore is then roasted, converting zinc and the impurity metals to their oxides. Heating the crude oxides with sodium chloride and coal converts germanium and other impurity metal oxides into their volatile chlorides. The chloride vapors are condensed and germanium chloride, GeCl_4 , is separated from the condensate by fractional distillation.

Germanium also is recovered from coal that contains this metal at trace concentrations. Coal ash and fine dusts are mixed with sodium carbonate, copper oxide, calcium oxide, and coal dust, and smelted. The crude oxide products are converted to their volatile chlorides. Germanium chloride is isolated from the condensate products by fractional distillation.

High purity (99.9999%) germanium may be produced by fractional distillation of the chloride in the presence of hydrochloric acid and chlorine in quartz stills, followed by hydrolysis of the purified chloride with double distilled water to produce germanium oxide, GeO_2 . The oxide is reduced with hydrogen at $1,000^\circ\text{C}$. Exceedingly high purity germanium for semiconductor applications may be obtained from the high purity grade material by the zone refining process. Impurities present in germanium are more soluble in its melt than the solid metal. Thus, repeated passes of a molten zone along the impure ingot of germanium effectively removes trace impurities from the solid metal ingot.

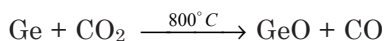
Doping of the metal for its solid state electronic use may be carried out either by adding trace amounts of doping agents into the melts before a single crystal is grown from the melt or into the prepared single crystal by solid state diffusion. Single crystals up to a few inches in diameter may be prepared from the melt by the Czochralski technique, which involves contacting the melt with a seed crystal under an inert atmosphere and controlled conditions of temperature and seeding.

Reactions

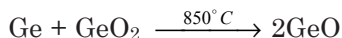
The chemical properties of germanium fall between those of silicon and tin. It forms both the divalent and tetravalent compounds, the oxidation state +4 being more stable than the +2 oxidation state. The metal is stable in air and water at ambient temperatures. However, it reacts with oxygen at elevated temperatures forming divalent and tetravalent oxides, GeO and GeO_2 .

While no reaction occurs with dilute mineral acids, the compound is attacked by concentrated HNO_3 and H_2SO_4 . Also, no reaction occurs with caustic alkalies.

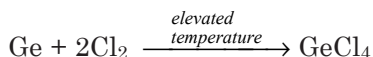
When heated with carbon dioxide at 800°C , the divalent oxide is formed:



The metal also reduces the tetravalent oxide to the divalent oxide upon heating at elevated temperatures:



Heating with chlorine at elevated temperatures yields germanium tetrachloride:



Analysis

The metal or its compounds may be digested with nitric acid, diluted appro-

priately and analyzed by flame or furnace AA or ICP emission spectrophotometry. It may also be analyzed by various x-ray methods, as well as ICP-MS.

GERMANIUM(IV) CHLORIDE

[10038-98-9]

Formula: GeCl_4 ; MW 214.40

Synonym: germanium tetrachloride

Uses

Germanium(IV) chloride is used in the preparation of many germanium compounds.

Physical Properties

Colorless liquid; density 1.879 g/cm³ at 20°C and 1.844 g/cm³ at 30°C; refractive index 1.464; boils at 86.5°C; solidifies at -49.5°C; decomposes in water; soluble in alcohol, ether, benzene, chloroform and carbon tetrachloride; insoluble in concentrated hydrochloric and sulfuric acids.

Thermochemical Properties

ΔH_f°	-127.1 kcal/mol
ΔG_f°	-110.6 kcal/mol
S°	58.7 cal/degree mol

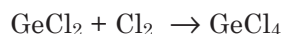
Preparation

Germanium(IV) chloride is prepared by reacting germanium metal with chlorine; or by treating germanium oxide, GeO_2 , with hydrochloric acid:



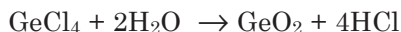
Germanium(IV) chloride often is obtained as a byproduct of germanium metal production. The process involves heating germanium oxide, GeO_2 , with sodium chloride and coal. The vapors of germanium(IV) chloride and other volatile chlorides formed from the impurity metals are condensed. The product is isolated by fractional distillation. Further purification may be achieved by fractional distillation in 8N HCl and chlorine, or in the presence of other oxidizing agents in quartz stills.

Germanium(IV) chloride also is obtained by chlorination of germanium(II) chloride at ambient temperature. The reaction is rapid.

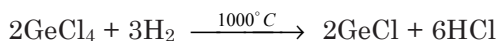


Reactions

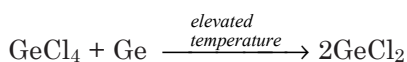
Germanium(IV) chloride reacts with water, hydrolyzing to germanium oxide and hydrochloric acid:



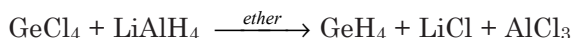
The rate of hydrolysis is slower than the corresponding silicon analog, with hydrolysis occurring only partially. When heated with hydrogen at 1,000°C in a quartz reactor, it is converted into germanium(I) chloride, condensing onto the wall of the reactor:



When vapors of GeCl_4 are passed over germanium at elevated temperatures, the product is germanium(II) chloride, GeCl_2 :

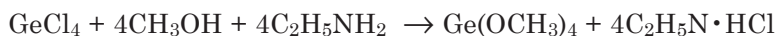


Reaction with lithium aluminum hydride in ether forms monogermane, GeH_4 :



Reactions with antimony trifluoride, SbF_3 in the presence of antimony pentachloride, SbCl_5 , form mixed halides of compositions: GeCl_3F , GeCl_3F_2 , GeCl_2F_2 , and GeClF_3 .

Reactions with alcohols in the presence of an amine yield alkoxides:



Germanium forms six coordinate adducts, such as $\text{GeCl}_4(\text{L})_2$ with many neutral ligands.

Analysis

Elemental compositions: Ge 33.86%, Cl 66.14%. The compound may be digested with nitric acid, diluted with water, and the diluted acid extract may be analyzed for germanium by AA and ICP spectrophotometry (See Germanium). The compound may be dissolved in a suitable organic solvent and analyzed by GC/MS. It may be identified from its molecular ions 212 and 220.

Toxicity

Fumes of germanium(IV) chloride irritate eyes, nose, and mucous membranes.

GERMANIUM DIOXIDE

[1310-53-8]

Formula: GeO_2 ; MW 104.61.

Synonym: germanium(IV) oxide

Uses

Germanium dioxide has high refractive index and infrared transmission, for which it is used in industrial glasses. It also is used in preparation of high purity grade germanium.

Physical Properties

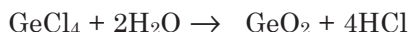
Germanium dioxide occurs in two crystalline and one amorphous modifications: (1) a tetragonal rutile form, refractive index 2.05, density 6.24 g/cm^3 at 20°C . (2) white hexagonal quartz modification, refractive index 1.735, density 4.70 g/cm^3 at 18°C , and (3) a glassy amorphous form, refractive index 1.607, density 3.64 g/cm^3 at 20°C . The tetragonal form is practically insoluble in water, while the hexagonal and the amorphous modifications have low solubilities; 0.45 and 0.52% respectively, at 25°C . Aqueous solutions are acidic due to formation of metagermanic acid, H_2GeO_3 . Hexagonal modification converts to a tetragonal crystal system when heated at 350°C in water under pressure. Both crystalline forms convert to a glass-like amorphous GeO_2 when heated at $1,100^\circ\text{C}$.

Thermochemical Properties

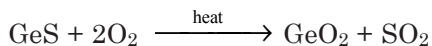
ΔH_f° (tetragonal)	-188.6 kcal/mol
ΔG_f° (tetragonal)	-124.6 kcal/mol
S° (tetragonal)	9.49 cal/degree mol
C_p (tetragonal)	12.45 cal/degree mol

Preparation

Germanium dioxide is prepared by heating germanium with oxygen at elevated temperatures, or by hydrolysis of germanium(IV) halides:



It also is prepared by oxidation of germanium(II) sulfide:

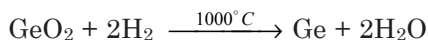


The product obtained in the above reactions is in the form of hexagonal modification of GeO_2 .

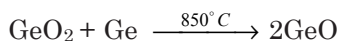
Reactions

Germanium dioxide is reduced to germanium metal when heated with

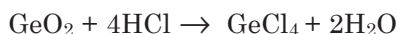
hydrogen at 1,000°C:



When heated with germanium, the dioxide is reduced to monoxide, GeO:



Treatment with hydrochloric acid yields germanium(IV) chloride:



In a strongly acidic solution, its reaction with hydrogen sulfide yields an amorphous modification of germanium(IV) sulfide, GeS₂.

Melting a mixture of germanium dioxide and metal oxides produces ortho- and metagermanates of the corresponding metals. Aqueous solutions of germanate react with molybdic and tungstic acids forming heteropoly acids of varying compositions.

Analysis

Elemental composition: Ge 69.41%, O 30.59%.

Germanium dioxide may be characterized by x-ray methods. Germanium metal may be analyzed in the acidified aqueous extract of the compound by AA, ICP, and other instrumental techniques (See Germanium).

GERMANIUM HYDRIDES

Germanium forms several tetravalent hydrides that have the general formula Ge_nH_{2n+2} similar to alkanes and silicon hydrides. The formulas and CAS Registry numbers of the three common hydrides are:

Name	CAS No.	Formula
Monogermane (the tetrahydride)	[7782-65-2]	GeH ₄
Digermane	[13818-89-8]	Ge ₂ H ₆
Trigermane	[14691-44-2]	Ge ₃ H ₈

Monogermane is used to produce high purity germanium metal. It also is used as a doping substance for electronic components.

Physical Properties

Monogermane is a colorless gas; density 3.43 g/L at 0°C; liquefies at -90°C; solidifies at -165°C; insoluble in cold and hot waters; soluble in liquid ammonia and sodium oxychloride; slightly soluble in hot hydrochloric acid.

Digermane, Ge_2H_6 is a colorless volatile liquid; density 1.98 g/mL at -100°C ; boils at 29°C ; decomposes when heated at 215°C ; solidifies at -109°C ; decomposes in water; soluble in liquid ammonia.

Trigermane is a colorless liquid; density 2.2 g/mL at 30°C ; solidifies at -105.6°C ; boils at 110.5°C ; insoluble in water; soluble in carbon tetrachloride.

Thermochemical Properties

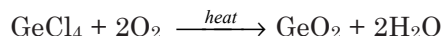
ΔH_f° ($\text{GeH}_4(\text{g})$)	21.70 kcal/mol
ΔH_f° ($\text{Ge}_2\text{H}_6(\text{l})$)	32.82 kcal/mol
ΔH_f° ($\text{Ge}_2\text{H}_6(\text{g})$)	38.80 kcal/mol
ΔH_f° ($\text{Ge}_3\text{H}_8(\text{l})$)	46.30 kcal/mol
ΔH_f° ($\text{Ge}_3\text{H}_8(\text{g})$)	54.20 kcal/mol
ΔG_f° ($\text{GeH}_4(\text{g})$)	27.10 kcal/mol
S° ($\text{GeH}_4(\text{g})$)	51.87 cal/degree mol
C_p ($\text{GeH}_4(\text{g})$)	10.76 cal/degree mol

Preparation

Polygermanes may be prepared by the reaction of magnesium germanide, Mg_2Ge , with dilute hydrochloric acid in an atmosphere of hydrogen. Monogermane, GeH_4 , may be prepared by various methods, such as: (1) Reduction of germanium tetrachloride, GeCl_4 , with lithium aluminum hydride in ether, (2) Electrolysis of a solution of germanium oxide, GeO_2 , in sulfuric acid using lead electrodes, and (3) Reaction of magnesium germanide and ammonium bromide, NH_4Br , in liquid ammonia.

Reactions

Germanium hydrides are less stable than the corresponding hydrides of carbon and silicon. Thermal decomposition produces germanium and hydrogen. Monogermane decomposes at 350°C , while digermane and trigermane decompose to their elements at 210° and 190°C , respectively, at 200 torr. At elevated temperatures the hydrides dissociate, depositing mirror-like germanium crystals on container surfaces. Heating with oxygen yields germanium oxide, GeO_2 :



Analysis

Germanium hydrides are decomposed by nitric acid, diluted with water, and analyzed for metallic Ge (See Germanium). Monogermane is identified by GC/MS.

Toxicity

Monogermane is moderately toxic. Inhalation causes irritation of the respiratory tract. Chronic exposure can induce kidney and liver damage.

GOLD

[7440-57-5]

Symbol Au; atomic number 79; atomic weight 196.97; a Group IB (Group 11) coinage metal; electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^1$; oxidation states +1 and +3, state +3 is common and more stable; naturally occurring stable isotope Au-196, several radioactive isotopes are known from mass 186 to 203; most long-lived radioisotope is Au-195 ($t_{1/2}$ 200 days).

History, Occurrence, and Uses

Gold has been known to mankind since ancient times, retaining an unique position among all metals and even precious stones in terms of its value, glamour, and allure for possession. Gold is widely distributed in nature but in very low concentrations. Mostly it occurs in native form as metal or alloyed with silver, containing small amounts of copper. A few gold compounds are also found in nature which are mostly the tellurides, such as sylvanite $(\text{Au}, \text{Ag})\text{Te}_2$, petzite $(\text{Au}, \text{Ag})_2\text{Te}$, and calaverite, AuTe_2 . Gold also is found in pyrites and quartzes, as well as in many sands and gravels of riverbeds. Large deposits of gold have been detected on the ocean floor. The average concentration of gold in seawater is 4ng/L and its abundance in the earth's crust is 4 $\mu\text{g}/\text{kg}$.

The most important uses of gold are in jewelry and as a monetary standard. The metal has been in use for jewelry, ornaments, and decorative items throughout civilization. Gold bullion and coins have been used as a medium of exchange all over the world. Other uses include electroplating or gold plating of electronic components, such as diodes, heat shields, plugs, and printed circuits, for infrared reflectivity and corrosion resistance. Other uses are in dentistry, brazing alloys, and photography. Certain salts of gold are used in medical treatment.

Physical Properties

Yellow metal; face centered cubic crystals; lattice constant, a at 25°C 4.0786Å; density 19.3 g/cm³; hardness 2.5–3.0 (Mohs), 18.5 (Brinell); melts at 1,064°C; vaporizes at 2,856°C; electrical resistivity 2.051 microhm-cm at 0°C and 2.255 microhm-cm at 25°C; Young's modulus 11.2 $\times 10^6$ psi at 20°C (static); Poisson's ratio 0.52; thermal neutron capture cross section 98.8 barns; insoluble in almost all single acids or hydroxide solutions; dissolves in aqua regia.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (g)	87.5 kcal/mol
ΔG_f° (g)	78.0 kcal/mol
S° (cry)	11.3 cal/degree mol
S° (g)	43.1 cal/degree mol
C_p (cry)	6.07 cal/degree mol
C_p (g)	4.97 cal/degree mol

ΔH_{fus}	15.22 kcal/mol
Coeff. linear expansion (at 100°C)	$14.2 \times 10^{-6}/^{\circ}\text{C}$
Thermal conductivity (at 0-100°C)	0.74 cal/cm ² /sec/°C

Production

Recovery of gold mostly involves the combination of several processes, including smelting, flotation, amalgamation and treatment with alkaline cyanide. The ore is crushed, ground, and washed. Quartz rocks that have much lower density than the gold are removed by hydraulic separation. The ground ore is then treated with an alkaline solution of sodium or calcium cyanide. The solution is made alkaline by adding lime. The cyanide concentration may range between 0.01 to 0.05%. Gold dissolves in the solution forming gold(II) cyanide, $\text{Au}(\text{CN})_2$. The solution is filtered to remove solid matter, following which it is subjected to electrolysis. Alternatively, gold is recovered from cyanide solution by precipitation with zinc dust or aluminum.

Gold flakes trapped in the ground ore may be recovered by amalgamation. Mercury and water are added to the ore and the mixture is passed over mercury-coated copper plates. Gold forms an amalgam with mercury and the amalgam adheres to the copper plates. Amalgam is scrapped off the copper plates. Mercury is removed by distillation.

Gold obtained by the above method contains copper, silver and other impurity metals. These metals are removed by melting, oxidation, electrolysis or chemical treatment. One such chemical refining is the Miller process in which chlorine gas is bubbled through molten impure gold. Most impurity metals volatilize as chlorides. Silver converts to silver chloride which remains in molten state at this temperature and may be decanted out. This refining process may upgrade gold to 99.5% purity. Other chemical processes for refining scrap and bullion involve precipitation of gold using ferrous sulfate, sulfur dioxide or other reducing agents.

Electrolytic refining yields a higher level of purity, over 99.95%. In electrolytic refining, the electrolyte is gold chloride mixed with HCl (about 5-10% free acid). During melting and oxidation of impure gold, silver alloys with the gold. The gold-silver alloy serves as the anode in electrolysis. An AC current is superimposed on the DC current to prevent any silver chloride buildup on the anode. Gold is deposited on the cathode during electrolysis. Copper, palladium, and platinum dissolve in the electrolyte solution as chlorides. Other impurity metals remain with the silver chloride residue.

Reactions

Gold is relatively inert in comparison to the other two coinage metals of Group IB; copper and silver. It also is chemically more inert than most other metals in the Periodic Table. It does not combine with oxygen, sulfur or selenium even at elevated temperatures. However, it reacts with tellurium in molten state forming gold telluride.

Gold reacts with chlorine, bromine and iodine at elevated temperatures forming the corresponding halides. Reaction with fluorine is very slow. In the presence of moisture, gold reacts with chlorine, bromine and iodine at ordi-

nary temperatures.

Gold is not attacked by most mineral acids including cold or hot sulfuric acid, phosphoric acid, hydrochloric acid and nitric acid. It dissolves in aqua regia or hydrochloric acid-nitric acid mixtures forming chloroauric acid, HAuCl_4 . The reaction does occur in hydrochloric-, hydrobromic- or hydriodic acid, in the presence of an oxidizing agent that would liberate nascent halogen, thus forming the corresponding gold halides.

Analysis

Gold may be identified by its physical properties. Trace quantities of gold may be analyzed by flame atomic absorption spectrophotometry (to 1 ppm) or by neutron activation analysis (to 1 ppb). The metal may be dissolved in aqua regia and the solution diluted appropriately prior to analysis. The most sensitive wavelength for this element is 242.8nm.

The following colorimetric analytical method may be applied: The metal is converted to its chloride by reaction with chlorine gas in the presence of moisture. Gold chloride so formed is reduced to colloidal gold by treatment with stannous chloride. Stannous chloride is oxidized to $\text{H}_2\text{Sn}(\text{OH})_6$, which deposits on the colloidal gold particles producing a beautiful ruby red color. The absorbance may be measured at 380 nm by a spectrophotometer and the concentration then determined from a standard calibration curve. Other color forming reagents, such as rhodanine, rhodamine or malachite green may be used. The colored complex of gold that is formed is separated from impurities in the aqueous solution by an appropriate organic solvent, and the absorbance of the solution is measured at 380nm.

Titrimetric methods also measure gold in solution. Gold(III) may be reduced by excess hydroquinone which may be back titrated with a standard solution of cerium(IV) titrant. Gold(III) may also be determined by iodometric titration.

GOLD(I) CHLORIDE

[10294-29-8]

Formula: AuCl ; MW 232.42

Synonyms: aurous chloride; gold monochloride

Physical Properties

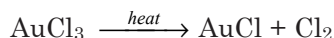
Yellow orthorhombic crystals; density 7.6 g/cm³; decomposes on heating at about 298°C; loses its stoichiometric composition at 170°C; very slightly soluble in cold water; decomposes in hot water; soluble in hydrochloric and hydrobromic acids, and alkali cyanide solutions.

Thermochemical Properties

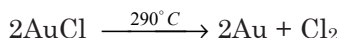
ΔH_f° -8.4 kcal/mol

Preparation

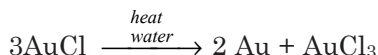
Gold(I) chloride is prepared by thermal decomposition of gold trichloride:

**Reactions**

When heated at 290°C, gold(I) chloride decomposes to gold and chlorine gas:



When heated with water, the compound decomposes to metallic gold and gold trichloride:



Reaction with potassium bromide yields potassium auric bromide and potassium chloride with separation of metallic gold:

**Analysis**

Elemental composition: Au 84.76%, Cl 15.24%. Gold(I) chloride is digested in hydrochloric-nitric acid mixture and the acid extract may be diluted and analyzed for gold (see Gold).

GOLD(III) CHLORIDE

[13453-07-1]

Formula: AuCl_3 ; MW 303.33; exists as a dimer, Au_2Cl_6 in solid and vapor state; forms a dihydrate, $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$

Synonyms: gold trichloride; auric chloride.

Physical Properties

Red monoclinic crystals; deliquesces; density 4.7 g/cm³; sublimes at 180°C (760 torr); highly soluble in water; soluble in alcohol and ether; slightly soluble in liquid ammonia.

Thermochemical Properties

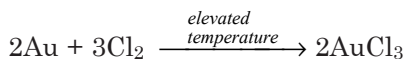
$$\Delta H_f^\circ (\text{AuCl}_3) \quad -28.1 \text{ kcal/mol}$$

$$\Delta H_f^\circ (\text{AuCl}_3 \cdot 2\text{H}_2\text{O}) \quad -170.9 \text{ kcal/mol}$$

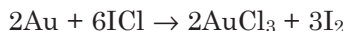
Preparation

Gold(III) chloride may be produced by the combination of metallic gold with

chlorine gas at elevated temperatures:



It may be prepared in the laboratory by the reaction of iodine monochloride with metallic gold:



The compound should be stored tightly closed and protected from light.

Reactions

When heated at 254°C, gold(III) chloride decomposes to gold(I) chloride and chlorine.

Passing hydrogen sulfide into an ether solution of the compound yields gold(III) sulfide, Au_2S_3 .

A similar reaction occurs when alcoholic solutions of gold(III) chloride and hydrogen selenide are mixed, producing gold(III) selenide, Au_2Se_3 , a black amorphous solid.

Gold(III) chloride may be reduced readily to metallic gold by common reducing agents. Thus, reduction with stannous chloride in dilute aqueous medium yields colloidal gold in which the atom carries a negative charge. "Cassius purple" is produced from the oxidation of tin to form $\text{H}_2\text{Sn}(\text{OH})_6$, which protects colloidal gold from coagulation, imparting ruby red color to the solution.

Gold(III) chloride reacts with ammonia forming a gold(III)-nitrogen derivative, an explosive product, known as, "fulminate of gold".

Reaction with Grignard reagent, RMgX in ether yields dialkyl gold(III) chloride, R_2AuCl_3 , which may be converted readily to other dialkyl gold(III) complexes by replacement of the chloride anion by a donor ligand.

Analysis

Elemental composition: Au 64.94%, Cl 35.06%. The aqueous solution may be analyzed for gold by AA spectrophotometry (see Gold). Chloride ion may be determined by chloride ion-selective electrode or ion chromatography. The solution must be diluted sufficiently for these measurements. Colorimetric methods are not suitable because the solution itself is colored.

GOLD CHLOROHYDRIC ACID

[16903-35-8]

Formula: HAuCl_4 ; MW 339.81; exists as tetrahydrate, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$; MW 411.85 Synonyms: chlorauric acid; aurochlorohydric acid; hydrochlorauric acid; gold trichloride acid; hydrogen tetrachloroaurate(III).

Uses

Gold chlorohydric acid is used for electroplating of gold; in porcelains and ruby glasses; and in photography.

Physical Properties

Tetrahydrate is golden yellow monoclinic crystals; hygroscopic; density 3.9 g/cm³; decomposes on strong heating; very soluble in water and alcohol; soluble in ether.

Preparation

Gold chlorohydric acid is prepared by treating gold with hydrochloric acid in the presence of chlorine:

**Toxicity**

Moderately toxic by ingestion. Skin contact can cause blisters.

GOLD(I) CYANIDE

[506-65-0]

Formula: AuCN; MW 222.98

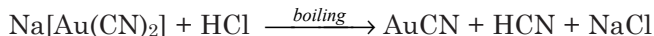
Synonyms: gold monocyanide; aurous cyanide

Physical Properties

Yellow hexagonal crystals; odorless; density 7.14 g/cm³; decomposes slowly in the presence of moisture or decomposes on heating; insoluble in water, alcohol and ether; also insoluble in dilute acids; soluble in aqueous solutions of potassium-, or sodium cyanide, ammonia, and aqua regia.

Preparation

Gold(I) cyanide may be prepared by boiling sodium aurous cyanide, Na[Au(CN)₂] with hydrochloric acid:



The complex cyanide, Na[Au(CN)₂] is made by dissolving gold in a dilute solution of sodium cyanide in the presence of air; or by dissolution of a gold anode in a solution of sodium cyanide during electrolysis. The solution is evaporated to separate the complex, Na[Au(CN)₂], which is purified by recrystallization from water. Potassium cyanide may be used instead of sodium cyanide to prepare gold(I) cyanide.

Analysis

Elemental composition: Au 88.34%, C 5.38%, N 6.28%. The compound may

be digested in nitric acid, diluted with water and the solution analyzed for gold (see Gold).

GOLD(III) FLUORIDE

[14720-21-9]

Formula: AuF_3 ; MW 253.96; fluoride bridge structure consisting of AuF_4 units.

Synonyms: gold trifluoride; auric fluoride

Physical Properties

Orange-yellow hexagonal crystal; density 6.75 g/cm³; sublimes at 300°C; decomposes at 500°C.

Thermochemical Properties

ΔH_f° -86.9 kcal/mol

Preparation

Gold(III) fluoride is prepared by fluorination of gold(III) chloride, AuCl_3 (or Au_2Cl_6), at 300°C. Either fluorine gas or hydrogen fluoride may be used as a fluorinating agent.

Analysis

Elemental composition: Au 77.56%, F 22.44%. Gold(III) fluoride may be characterized by x-ray techniques. The concentration of gold may be determined by AA and other instrumental methods following digestion in aqua regia and appropriate dilution.

GOLD(III) HYDROXIDE

[1303-52-2]

Formula: $\text{Au}(\text{OH})_3$; MW 247.99

Synonyms: gold trihydroxide; auric hydroxide.

Uses

Gold(III) hydroxide is used for decorating ceramics, porcelains and glasses. It also is used in gold plating solutions.

Physical Properties

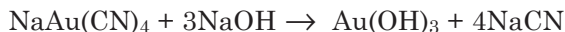
Brown powder; decomposes at 100°C; insoluble in water; soluble in acid.

Preparation

Gold(III) hydroxide is precipitated by mixing aqueous solutions of potassium auric chloride and sodium carbonate:

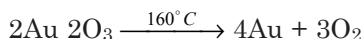
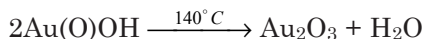
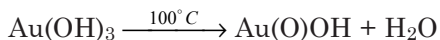


The product usually contains about three molecules of water of crystallization. It may alternatively be prepared by adding caustic soda solution to sodium auric cyanide:



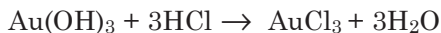
Reactions

Heating the hydroxide at about 140°C yields gold(III) oxide which on further heating decomposes to metallic gold and oxygen:



It also decomposes to metallic gold on exposure to sunlight.

Reaction with concentrated hydrochloric acid yields gold(III) chloride:



Reaction with ammonia forms gold fulminate, which explodes when dry.

Analysis

Elemental composition: Au 79.44%, H 1.22%, O 19.35%. The hydrated salt containing three water molecules has 65% gold. The compound may be acid digested, diluted appropriately, and analyzed for gold by various instrumental methods (see Gold).

GOLD(III) OXIDE

[1303-58-8]

Formula: Au_2O_3 ; MW 441.93

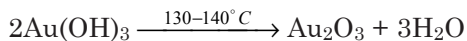
Synonyms: auric oxide; gold trioxide; gold oxide; gold sesquioxide

Physical Properties

Brown powder; decomposes slowly on exposure to sunlight or by heating at 150°C; begins to release oxygen at 110°C; fully decomposes to metallic gold at 250°C; insoluble in water; soluble in hydrochloric and concentrated nitric acids; also soluble in aqueous solutions of sodium- or potassium cyanide.

Preparation

Gold(III) oxide is prepared by heating gold(III) hydroxide, $\text{Au}(\text{OH})_3$ at 130 to 140°C:

**Analysis**

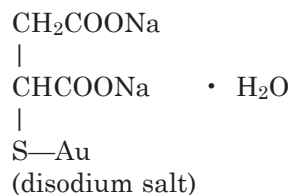
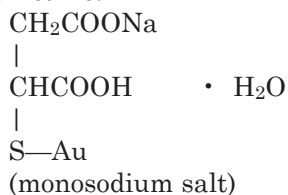
Elemental composition: Au 89.15%, O 10.86%. Gold(III) oxide is acid digested, the acid extract diluted appropriately with water and analyzed for gold by atomic absorption spectrophotometry or other instrumental techniques (see Gold).

GOLD(I) SODIUM THIOMALATE

[12244-57-4]

Formula: Gold(I) sodium thiomalate is a mixture of monosodium- and disodium-salts of gold thiomalate; the respective molecular formulas being $\text{C}_4\text{H}_4\text{AuNaO}_4\text{S}$ (monosodium salt) and $\text{C}_4\text{H}_3\text{AuNa}_2\text{O}_4\text{S}$ (disodium salt); a tetrameric structure with S—Au—S linear units.

Structure:



Synonyms: sodium aurothiomalate; mercaptobutanedioic acid monogold (1+) sodium salt; Myochrysine; Mycocrisin; Shiosol

Uses

The compound is a drug for the treatment of rheumatoid arthritis. The mode of transport of this drug in the body involves the exchange of thiomalate ligands *in vivo* and the binding of Au(I) to $-\text{SH}$ and S—S units of proteins, such as blood serum albumin.

Physical Properties

White to yellowish white powder; odorless; metallic taste; highly soluble in water; practically insoluble in ethanol and ether.

Preparation

Gold(I) thiomalate is prepared by reacting sodium thiomalate with gold(I) halide. It is stored in the dark and otherwise protected from light.